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Study of the Production of Some Superconducting and Magnetic
Materials by Solidification in the Drop Tube and Drop Tower

by

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PURPOSE AND BACKGROUND:

The purpose of this study is to carry out a systematic study on the relationship between the microstructure and physical properties of several superconducting materials prepared by solidification in low gravity. Further study of the materials, such as the application of hydrostatic pressure which is known to be an effective mean to vary the electronic structure of materials, in conjunction with the detailed microstructure analysis of the samples is also performed to better understand the low gravity effects on the enhancement of the electronic properties.

The feasibility of producing high volume fraction immiscible alloys with finely dispersed microstructure by low-gravity solidification was demonstrated in 1974.[1] Ga-Bi samples solidified in free fall, with gravity level $10^{-4}g$ ($g = 980$ cm/sec), [2] had much finer microstructure than the control samples solidified in normal gravity. It was also found that the electrical properties of the low-gravity solidified materials were significantly different from those of the control samples solidified under at the same conditions except at one gravity. The potential to synthesize in space a new class of electronic materials was suggested by these initial experiments.

However, extensive studies along this line in space are limited due to the high cost and limited access to orbital ex-

perimentation facilities. In an attempt to gain more insight into the low-gravity processing on the material properties of immiscible alloys, we decided to carry out a systematic study of materials solidified directionally in a Bridgman furnace on NASA's KC-135 aircraft. The advantages of using KC-135 are that it is relatively inexpensive, has a short turnaround time, and provides the capability when combined with unidirectional solidification of having in one sample a series of identifiable sections grown in low-g or high-g.[3-5] The material chosen in this study is the ternary Al-In-Sn alloy. [6]

On the other hand, several important questions concerning the relation between the fine microstructure and cooling rate,[1] droplet size [7] and the proper choice of material in terms of interfacial energy have been raised.[8] Furthermore, although the observation of the anomalous electric properties in low gravity processed GaBi samples has been related to the fine microstructure due to the fine dispersion of Ga particles in Bi matrix, a complete understanding of the behavior is still not available.

In an effort to understand better some of the questions mentioned and the low gravity effects on the physical properties of an immiscible alloy in general, we decided to carry out experiments to solidify immiscible GaBi alloys in drop-tower using a new package which allows us to have better control in parameters such as cooling rate and sample size.

It is known that the application of pressure one of the simplest and most direct approach in characterizing electronic

properties of solids,[9] since various interactions, responsible for the great diversity of solid behavior, depend on the interatomic distance. It is also known that pressure can effectively modify the material properties which may be related to the interfacial phenomena. Therefore, we also carried out measurements on the physical properties of the prepared samples under pressure.

In the following, we present results of the studies on the directionally solidified Al-In-Sn alloys processed in KC-135 airplane and immiscible GaBi alloy prepared during free fall in Marshall Space Flight Center Drop Tower.

I. DIRECTIONALLY SOLIDIFIED Al-In-Sn ALLOYS

A photomicrograph of Al-18.9In-14.6Sn flight sample for which properties data are reported here is shown in Figure 1. Typical resistance R of samples solidified at different gravity levels are shown in Figure 2 as a function of temperature. It can be seen that the resistance of low- g samples is less temperature dependent. In Table I, we summarize the electrical properties of the samples measured which include the sample section prior to directional solidification and In-Sn alloys of two selected compositions. Figure 3 is a schematic plot showing resistance as a function of temperature for typical semi-metal and metal with a superconducting transition at low temperature. Results given in Figure 2 in comparison to the characteristic curves in Figure 3 clearly indicate that the low- g sample behaves more like a semi-

metal while the high-g sample is essentially metallic.

All samples studied become superconducting with an onset temperature ranging from 7.8 K to 6.3 K. Figure 4 shows the temperature dependence of the resistance and magnetic susceptibility at low temperature for a high- and low-g section. The average transition width is 3 K, showing the inhomogeneous character of our material. T_c , resistance ratio, and the gravitational acceleration parallel to the growth axis during solidification as plotted versus sample position is shown in Figure 5.

In Figure 6, we have shown the detailed resistive behavior of the sample at low temperature. An unusual electrical anomaly is observed for both low-g and high-g samples in the temperature regime right before the complete superconducting transition. The resistance first decreases on cooling and then suddenly rises before the complete transition. The magnitude of the anomaly depends on the measuring currents. Such an anomaly was not observed in the ground processed In-Sn samples.

Microstructure and chemical composition analyses of the samples have been performed using SEM fitted with a WDX analyzer. The micrographs clearly show that the samples consist of particles of 3 - 50 μm in size embedded in the aluminum matrix. It is found that there are two different phases in these particles, viewed as dark and light particles in the light field SEM. The apparent volume fraction of the dark phase is about one-third of the particles. These particles are made almost entirely of In

and Sn. The dark phase of the particles consists of In-Sn with 25 wt.% Sn and the Sn content does not change with g-level during solidification. On the other hand, the Sn concentration of the light phase of the particles does appear to vary with gravity level. The low-g light particle is mainly In-Sn with 25 wt.% Sn, while its counterpart in high-g is mainly In-Sn with 75 wt.% Sn. A summary of the results is also given in Table I.

The results given in Table I and Figure 5 clearly demonstrated that the accelerations during solidification greatly affect the electrical properties of the sample. The resistivities of the samples are dominated by the scattering of electrons by the dispersion of second phase which is the precipitated In-Sn embedded in the aluminum matrix if we consider the connecting path of the electron is the aluminum matrix. It is known that the electrical properties of an alloy depend on its particle size and the interface between particles.[10] Smaller particles will lead to an increase in the surface-to-volume ratio with a subsequent increase in electron scattering and interface effects. The relatively smaller resistance ratio and the larger room temperature resistivity of the low-g sample over those of the high-g samples suggest that samples solidified at low-g may consist of finely dispersed particles. Unfortunately, we do not see any clear difference in particle size between low-g and high-g samples from photomicrographs. This suggests that the conducting path may be different for samples solidified at different gravity level.

Based on the WDX composition analysis, it can be inferred from the phase diagram that low-g samples contain mainly β phase (25 wt.%Sn) In-Sn particles, while the high-g samples consist of small portion of β phase particles randomly distributed in the larger Γ phase (75 wt.%Sn) particles. Therefore, we propose a model that for the high-g samples, the connectivity of the conducting path is through the aluminum matrix, and for the low-g samples, it is through the precipitated In-Sn particles. This model is shown schematically in Figure 7. The observation of the resistive behavior of the ground processed In-Sn samples, which is similar to that of the low-g samples but different from that of the high-g samples, seems to support such an assumption. In addition, a photomicrograph study of the deep etched sample indeed shows that the precipitated particles are more dense in the low-g sections than in the high-g sections, but attempts to quantitatively verify the difference in the connectivity of the In-Sn phase have been thus far inconclusive.

The superconductivity observed is attributed to the presence of the In-Sn phase. Superconductivity of the In-Sn system has been extensively studied.[11-13] It was found that T_c of the quenched samples varies from 7.8 K to 5.5 K with Sn content.[9] Peak T_c of 7.8 K occurs at the β phase with composition of 30 wt.% Sn, while Γ phase alloys have T_c on the order of 6 K. Superconducting transition temperature of In-Sn alloys as a function of Sn content along with the In-Sn binary phase diagram is shown in Figure 8. This is consistent with our observations that low-g samples have T_c about one degree higher than that of the

high-g samples, and our hypothesis based on WDX analysis that the low-g particles are essentially β phase, while high-g sections contain mainly Γ phase particles.

The resistive anomaly observed at low temperature is rather unusual. The dependence of the anomaly on transport currents and external magnetic fields indicates that the anomaly is superconducting in origin. It suggests that the sample undergoes a normal -- superconducting -- normal -- superconducting transition. It is known that a granular superconductor, in which the superconducting grains are coated with an insulating layer or embedded in an insulating matrix, may exhibit re-entrant superconductivity.[14-16] In view of the inhomogeneous nature of our sample, it is very possible that there exist small superconducting grains coated with thin insulating film that have relatively larger T_c than that of the major In-Sn particles. At this moment, whether the exact origin of this superconductivity is due to the In-Sn micrograins or some unidentified phases (such as interfacial effects [17] between particles) is unknown. The absence of the anomaly in the ground processed In-Sn samples suggests that the presence of aluminum may play an important role.

In conclusion, we have studied the ternary, Al-18.9In-14.6Sn directionally solidified in NASA KC-135 aircraft. Electrical properties measurements of the samples solidified at different g-levels show that: (1) low-g samples behave more like a semi-metal while high-g samples are essentially metallic. (2) Both low-g and high-g samples are superconducting but T_c of low-g samples is 1 K higher than that of high-g samples. (3) A resistive anomaly at-

tributed to re-entrant superconductivity is observed in the samples studied.

II. IMMISCIBLE GaBi ALLOY

The normalized temperature dependence of resistances at different pressures for the drop-tower (DT) and ground control (GC) samples are shown in Figure 9. As temperature decreases, R exhibits a broad maximum at 100K for DT sample, but decreases continuously for GC sample. The residual resistivity of the DT sample is found to be $70 \mu\Omega\text{-cm}$. Compare this value with the results by Otto and Lacy,[2] the average particle size of our sample is estimated to be about $1.5 \mu\text{m}$. However, at low temperature, both resistive and magnetic susceptibility measurements show that there are two superconducting transitions for DT sample. A transition with higher temperature (T_{c1}) occurs at 8.4K, and a lower one (T_{c2}) at 7.7K. In Figure 10 we show the detailed low temperature resistivity and susceptibility data at three pressures. It is apparent that both superconducting phases are non-bulk. The lower T_c transition has larger volume fraction which is 3%, while the higher T_c phase has only a volume fraction 0.1%. In the GC sample, only one transition at T_{c2} (7.7K) is observed. In order to find such an observation is a general result, we re-examine some of the samples studied previously. It indeed shows that the samples prepared under low gravity condition all exhibits two superconducting phases. While only one detectable transition is observed in the samples processed at normal gravity.

The application of pressure is found to have different effects on the overall resistance of the DT and GC samples. As summarized in Table II, for DT sample, the resistance first increases as pressure increases, reaches a peak at 7 kbar, and then decreases as pressure further increases. The temperature dependence of R behave similarly under pressure, as evidenced in Figure 11. The negative temperature dependence of R for DT sample becomes more prominent as pressure increases until the pressure is larger than 10 kbar. This results can also be seen in the appearance of peak activation energy value B with pressure at 10 kbar. More interesting is that T_{c1} of DT sample also varies non-monotonically with pressure as shown in Figure 11. However the peak of T_{c1} is at about 5 kbar which is lower than that of R and dR/dT . On the other hand, T_{c2} of DT sample decreases almost linearly with pressure. The pressure coefficient of T_{c2} is found to be -3.2×10^{-5} K/bar.

For GC sample, the overall resistance decreases as pressure increases. An almost factor of 6 drop in resistance is observed at 2 kbar. This may be due to a phase transition of Bi from Bi-I to Bi-II. However, dR/dT value becomes smaller with increasing pressure, as evidenced by the ratio of overall resistance to residual resistance list in Table II and the curves shown in Figure 12. T_{c2} of GC sample behaves similarly to T_{c2} of DT sample with almost identical pressure coefficient.

It is well known that in a pure metal, phonon scattering results in a linear temperature dependent term in R at high temperature, and gives a T^5 dependence of R at temperature much lower than the Debye

temperature of the metal. On the other hand, in a highly disordered alloys, the resistance can have a strong negative temperature dependence resemble to that of a semiconductor or an insulator.[18] Such a metal-insulator transition has recently been observed in the Au-Ge alloy system with Au concentration less than 24 at.% where no crystalline state exists.[19]

In view of the fine dispersion of Ga particle in Bi matrix observed in DT samples, it is not impossible that in these samples a disordered or amorphous phase is formed and results in a semiconducting phase with relatively small energy gap at the interface. With such a consideration in mind, the observed resistance maximum in DT sample can be understood as the result of the competing effect of the metallic contribution in the matrix and the semiconducting phase at the interface. At high temperature, the mean free path of the electron is short, the semiconducting phase will dominate and give a negative dR/dT . This is consistent with the reduction in the number of free electron as temperature decreases derived from the Hall effect measurements on DT samples.[20] When the temperature further decreases, the mean free path of electron increases, and the metallic portion becomes dominant to give the rapid decrease in resistance.

Since the interface effect is expected to depend on the particle size, an optimum condition may exist for the formation of the disordered phase at the interface. By varying particle size or application of pressure can tailor such an optimum condition. The observation of the existence of peak values of the overall resistance, negative dR/dT , and activation energy B in DT sample can all be ex-

plained by the existence of such an optimum phase matching condition. In addition, the ever decreasing dR/dT value of GC sample with pressure is also consistent with such a suggestion.

The detection of two superconducting transition in DT sample but only one lower T_c transition in GC sample is surprising. From the existing data on superconducting elements and alloys which related to this study, it is found that only amorphous (thin film) Ga,[21] amorphous GaBi alloys [22] (Ga concentration larger than 80 percent), and Bi-VI (above 90 kbar pressure) can have T_c higher than 8 K.[23] The pressure effect on T_c of Bi-IV phase is found to be negative,[24] this is inconsistent with the non-monotonic variation of T_{c1} with pressure. Based on the suggestion that amorphous phase may exist at interface between Bi matrix and Ga particle, the observation of high T_c phase in DT sample can be due to the existence of amorphous Ga or amorphous GaBi alloy at the interface. However, other possibility such as the interfacial superconductivity [17] due to the presence of metal / semiconductor interface can not be ruled out at this moment. Since GC sample has coarse dispersion, formation of the highly disordered phase at the interface is not expected, high T_c phase is also not expected, consistent with our observation.

The lower T_c superconducting phase observed in both DT and GC sample has a pressure coefficient dT_c/dP -3.2×10^{-5} K/bar. This value is similar to that found in Ga-II and Bi-V phase.[24] However, the Bi-V phase exists only at pressure larger than 68 kbar and has a T_c w 6.7 K which is too small to account for our observation. Therefore, we can attribute the lower T_c phase to the presence of Ga-II phase in

both DT and GC samples.

The resistivity anomaly found in GaBi samples prepared with low gravity solidification can be attributed to the possible existence of amorphous or highly disordered phase in the interface between the Ga fine particle and Bi matrix. Two superconducting phases are observed in the low-gravity processed samples, while only one at lower transition temperature is detected in the ground control samples. The high T_c phase in DT sample can be due to the amorphous Ga phase, amorphous GaBi or some unknown phase due to novel superconducting mechanism. Detailed analysis using scanning tunneling microscope is planned to pin point the exact phase responsible for our observation. The lower temperature superconducting phase found in both DT and GC samples is identified with the Ga-II phase from the pressure measurement.

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TABLE I. ELECTRICAL PROPERTIES OF Al-18.9In-14.6Sn

Sample No.	$\rho(273\text{ K})$ ($\mu\Omega\text{-cm}$)	$\rho(273\text{ K})/\rho(T_c)$	T_c (K)	Sn Content (wt.%)		G
				(LPP)	(DPP)	
1	13.5	38.3	6.5	24	19	1
2	121.2	1.54	7.4	26	25	Low
3-1	9.3	25.4	6.7	72	19	High
3-2	103.2	7.9	7.1	22	19	Low
4	19.1	15.2	6.5	68	21	High
5	123.6	5.6	7.8	26	19	Low
6	14.9	4.7	6.7	50	21	High
7-1	731.7	0.78	7.3	21	26	Low
7-2	395.2	1.8	7.4	21	26	Low
8	15.5	13.9	6.5	73	26	High
9	46.7	2.4	7.3	-	-	Low
Al	1.17	4.2×10^3	1.17			
In ₇₅ Sn ₂₅ (β)	56.1	2.15	7.1			
In ₂₅ Sn ₇₅ (γ)	70.1	2.57	6.4			

LPP: Light Phase Particles

DPP: Dark Phase Particles

G: Level of Acceleration

Table II. Parameters of GaBi (both DT and GC) samples

Sample	P(kbar)	T _{c1} (K)	T _{c2} (K)	B(mev)	n	$\rho_0(\mu\Omega\text{-cm})$	$\rho_{RT}(\mu\Omega\text{-cm})$
GaBi (DT)	0	8.26	7.67	0.53	2.5	77.1	177
	0.4	8.32	7.58	0.28	2.0	37.4	99.3
	3.0	8.50	7.53	0.68	1.63	35.6	104.6
	7.1	8.48	7.42	0.88	1.98	47.5	134
	10.2	8.41	7.31	1.35	1.63	41.4	122.4
	14.0	8.27	7.18	0.29	1.96	32.9	103.5
	15.0	7.95	7.12	0.72	1.4	29.2	98.8
	16.5	7.7	7.12	0.43	1.3	20.2	96.7
	17.6	7.65	7.10	< 0	1.1	13.0	86.0
GaBi (GC)	0	--	7.66	--		1.35	72.6
	0.3	--	7.60	--		6.30	63.2
	1.6	--	7.57	--		1.40	11.4
	5.3	--	7.36	--		0.50	6.6
	7.8	--	7.27	--		0.30	3.5
	12.0	--	7.17	--		0.14	2.6
	15.3	--	7.15	--		0.23	2.7
	17.8	--	7.10	--		0.17	2.2

Al-18In - 14Sn MONOTECTIC ALLOY

DIRECTIONALLY SOLIDIFIED DURING KC-135 MANEUVERS

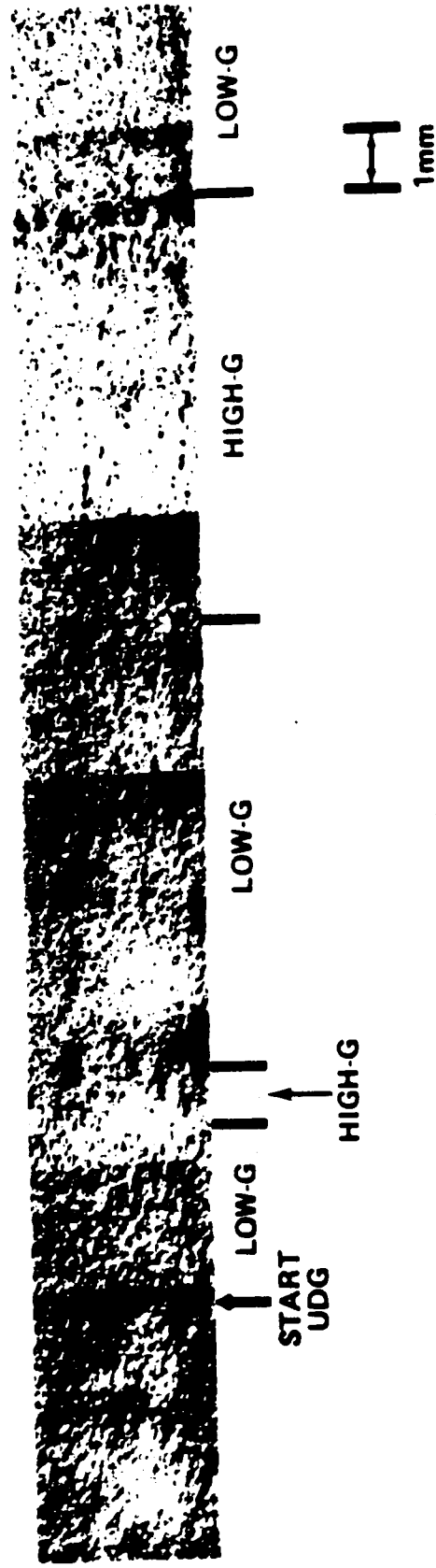


Figure 1. Photomicrograph of Al-18.9In-14.6Sn along the longitudinal growth axis showing the microstructure of the sample up to the third low-g zone.

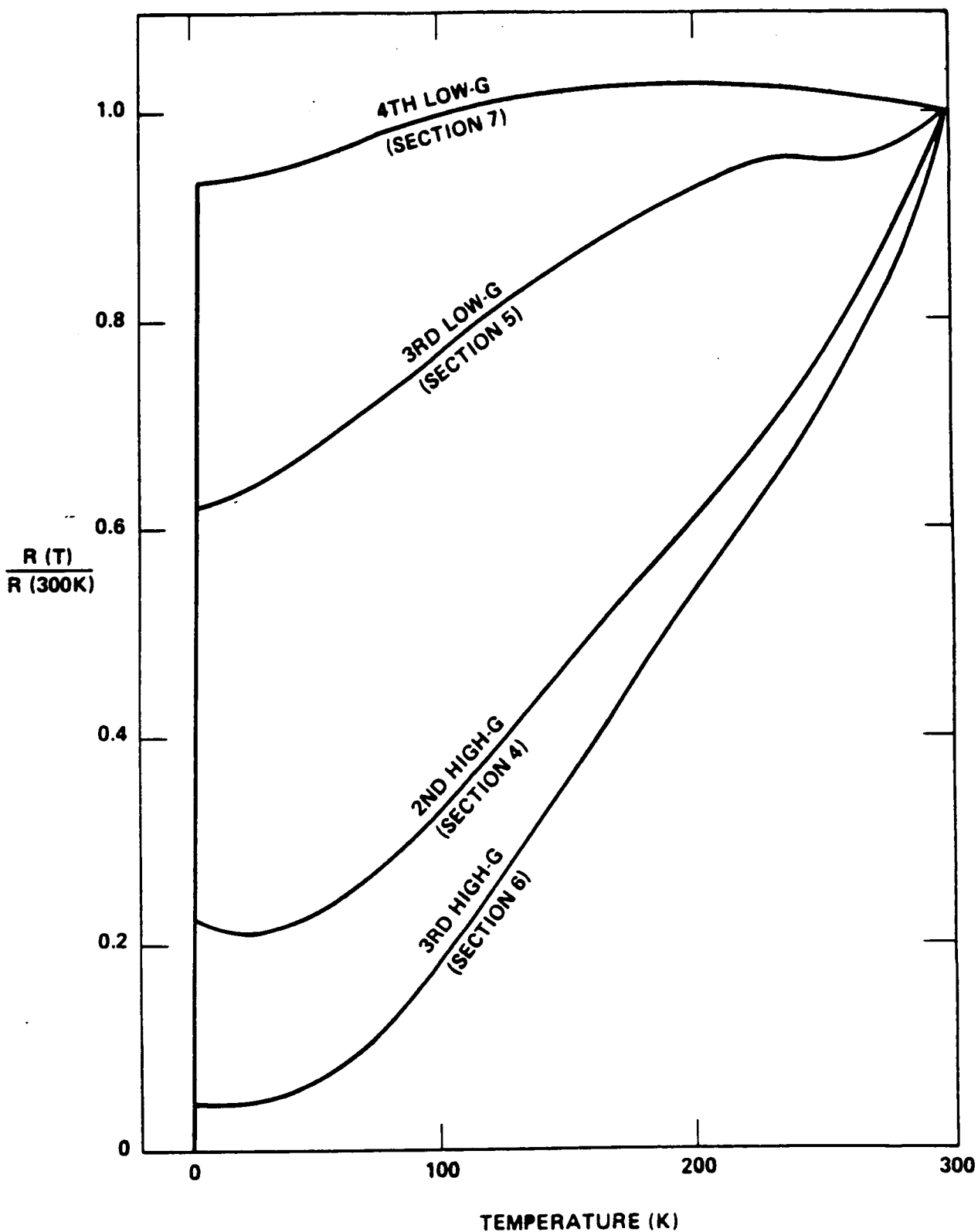


Figure 2. Normalized resistance $R(T_c)/R(300\text{ K})$ as a function of temperature of Al-18.9In-14.6Sn sections solidified under different levels of acceleration.

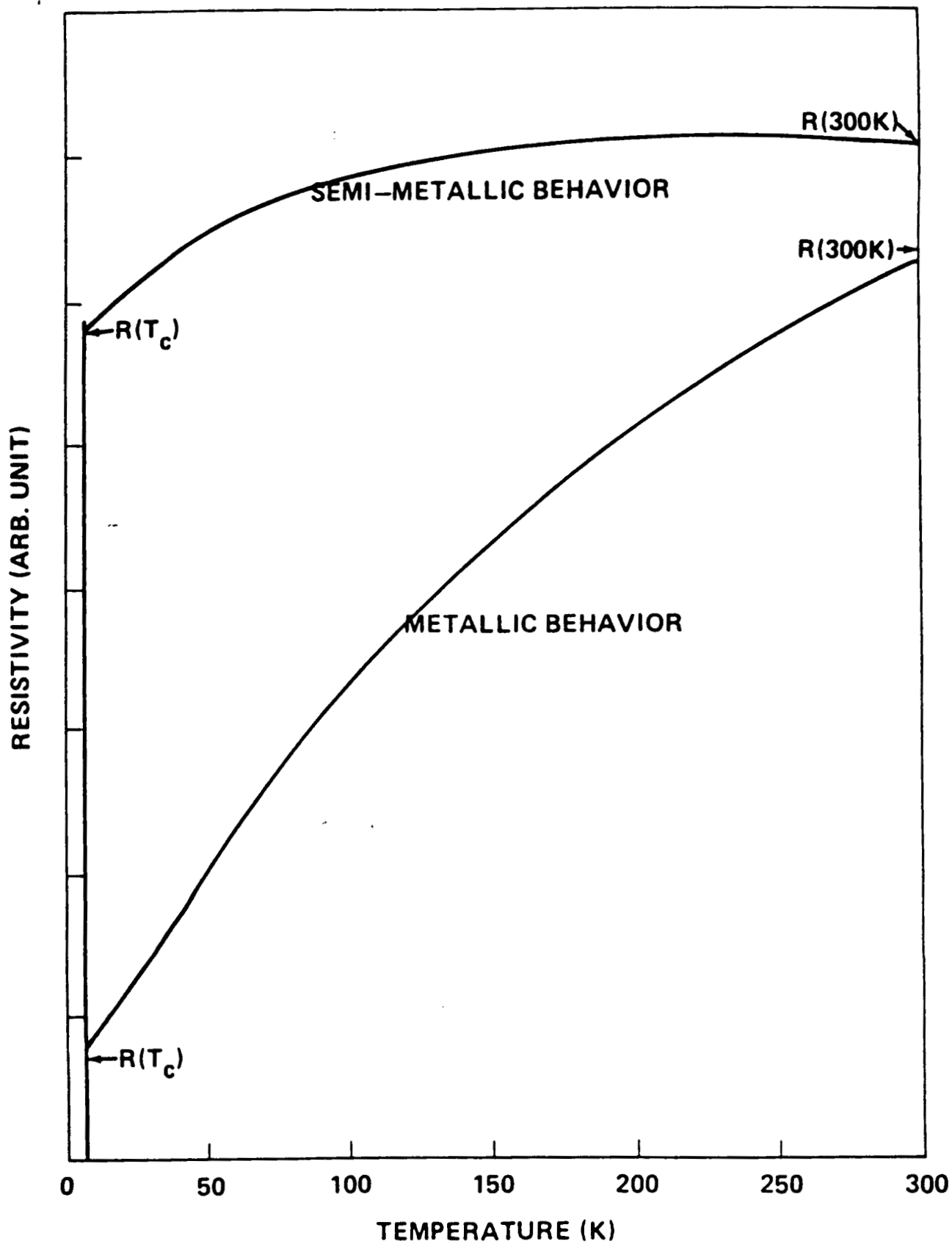


Figure 3. Schematic plot illustrating the characteristic behavior of resistance as a function of temperature for semi-metal and for metal with superconducting transition at low temperature.

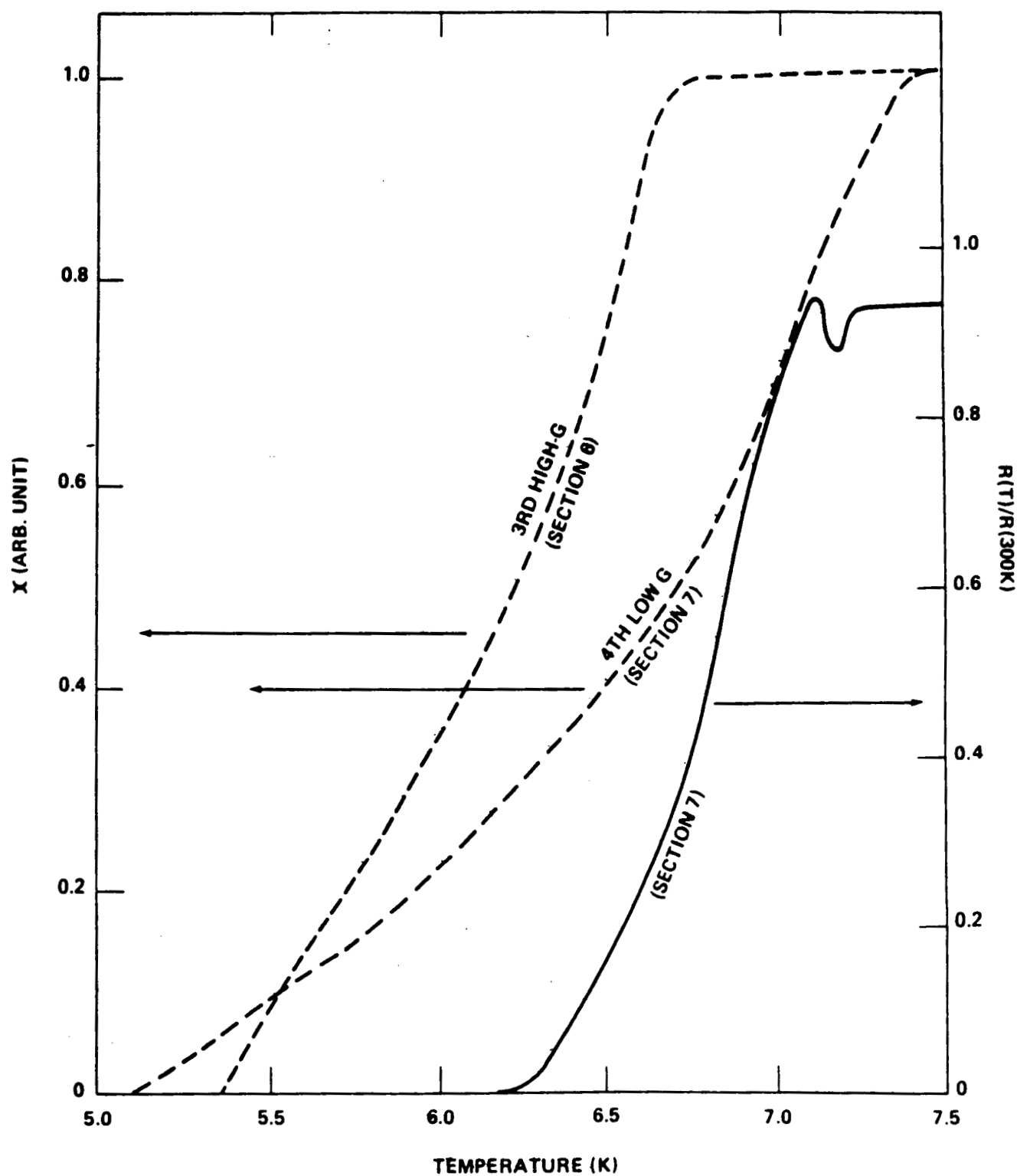


Figure 4. Electrical resistance and magnetic susceptibility at low temperature of Al-18.9In-14.6Sn solidified under different levels of acceleration.

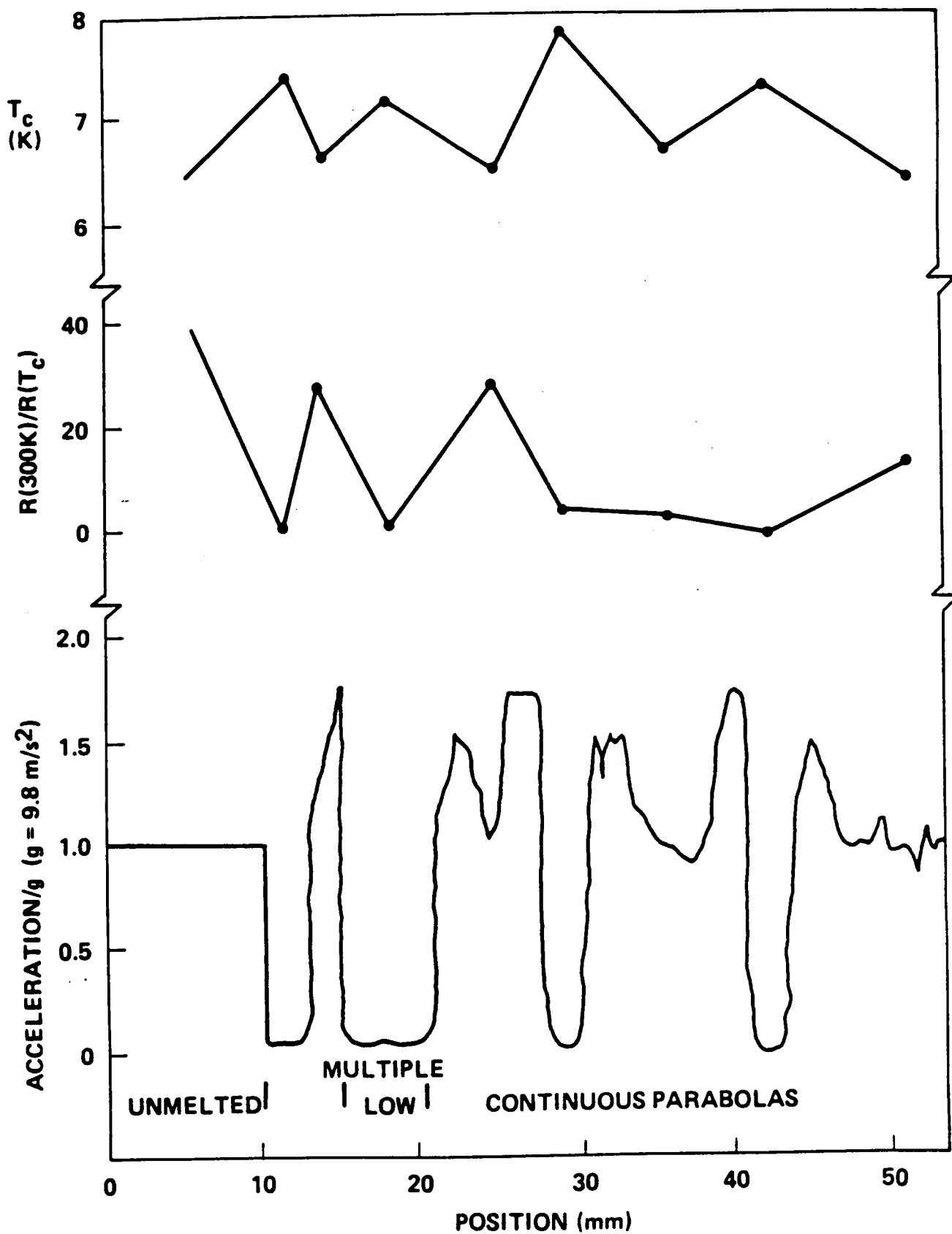


Figure 5. T_c , $R(300 \text{ K})/R(T_c)$, and gravitational acceleration along the longitudinal growth axis as a function of sample position.

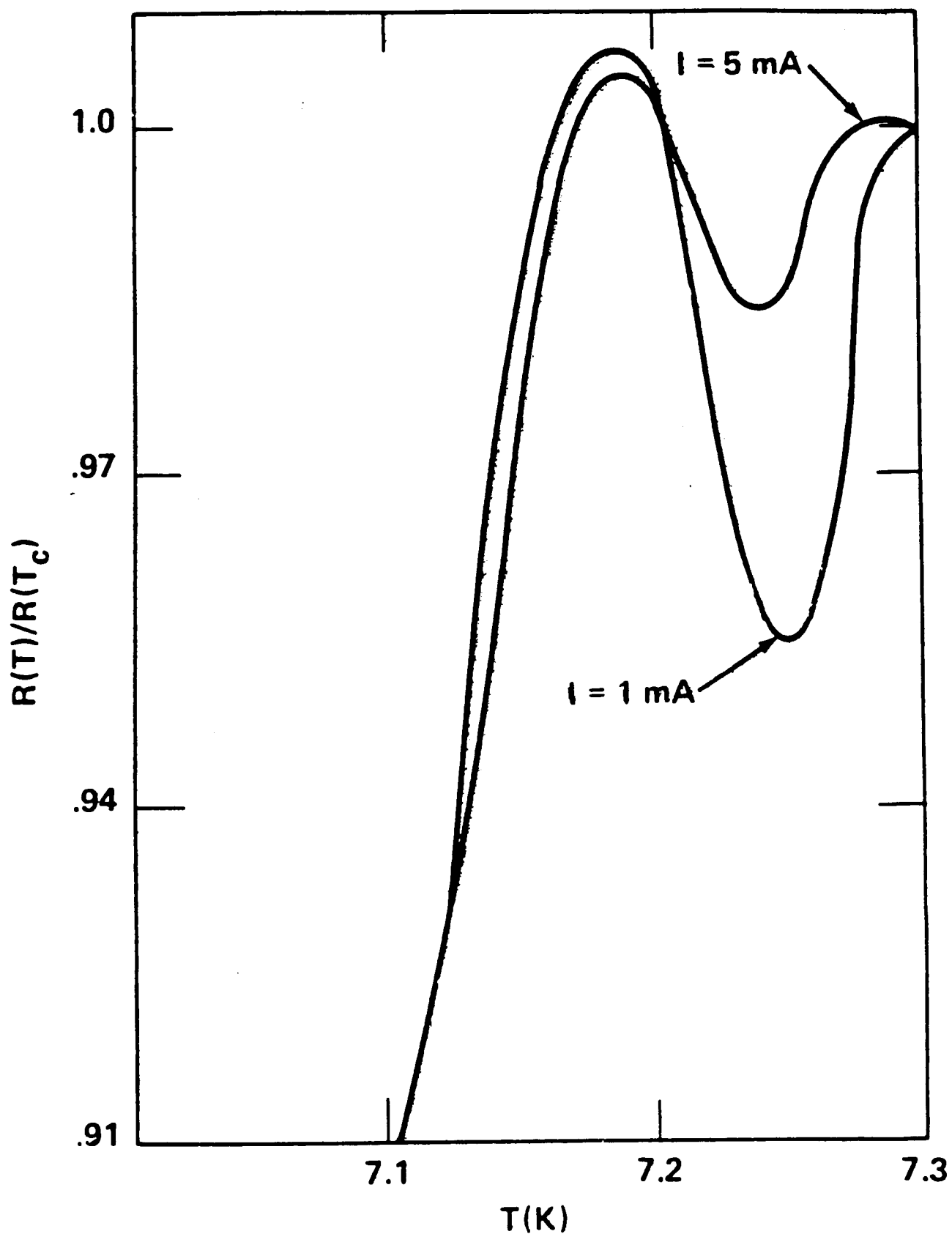


Figure 6. Detail of the electrical resistance as a function of temperature near the superconducting transition temperature, T_c , at two measuring currents.

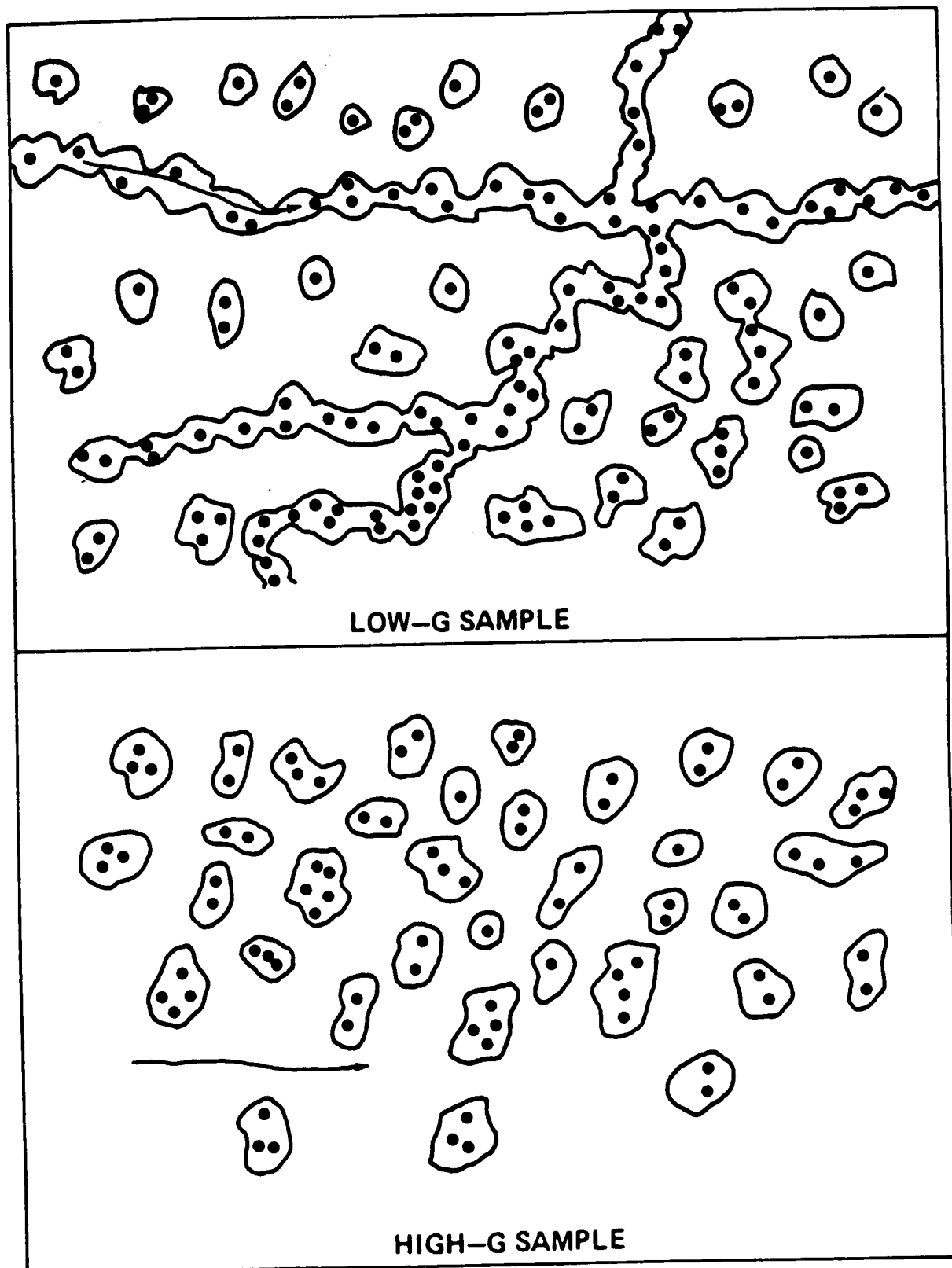


Figure 7. Schematic plot showing the proposed model for the current conducting path for sample solidified in low g and in high g.

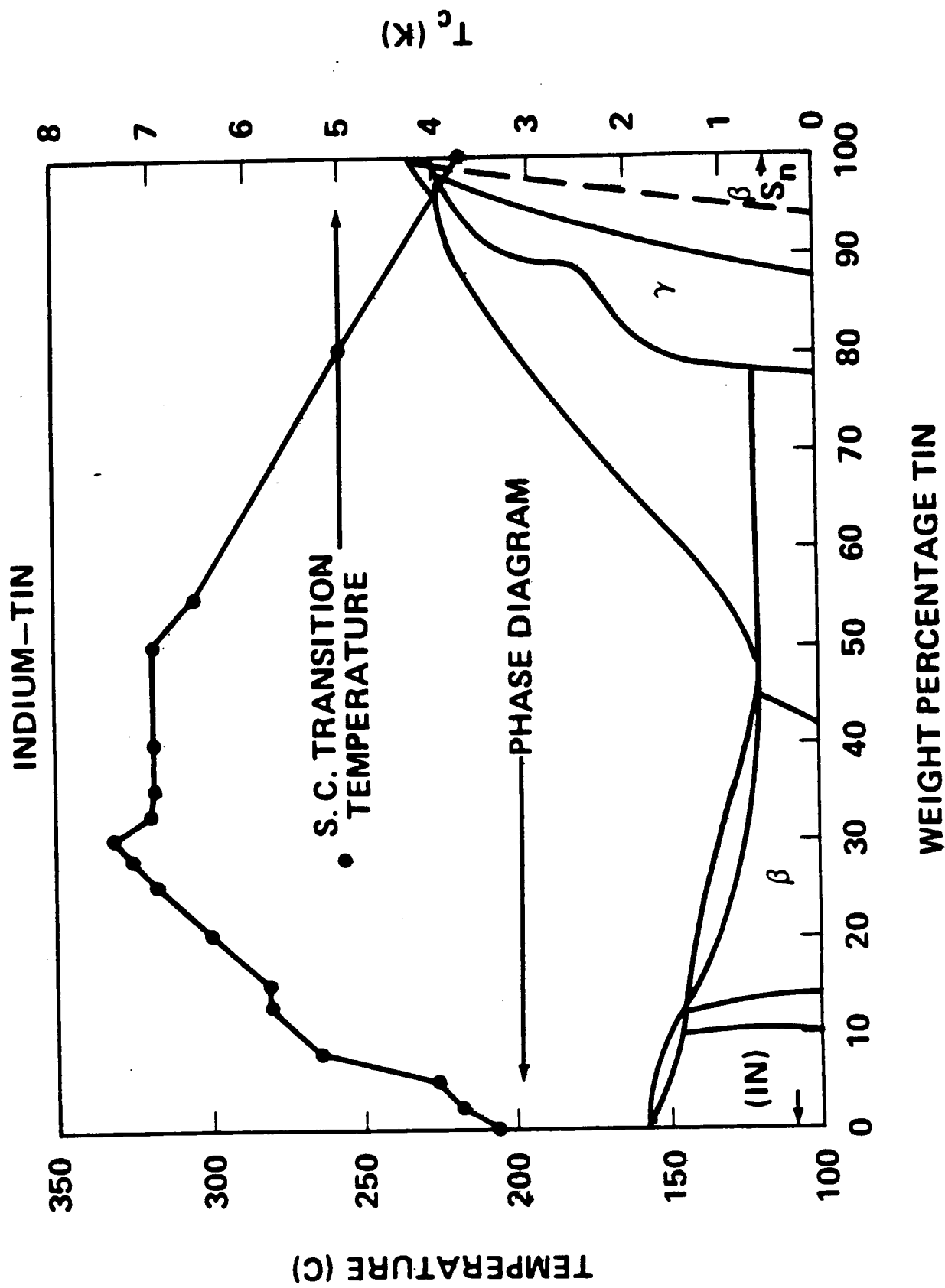


Figure 8. Superconducting transition temperature plotted versus Sn concentration and the phase diagram of In-Sn alloys (T_c data taken from Reference 9).

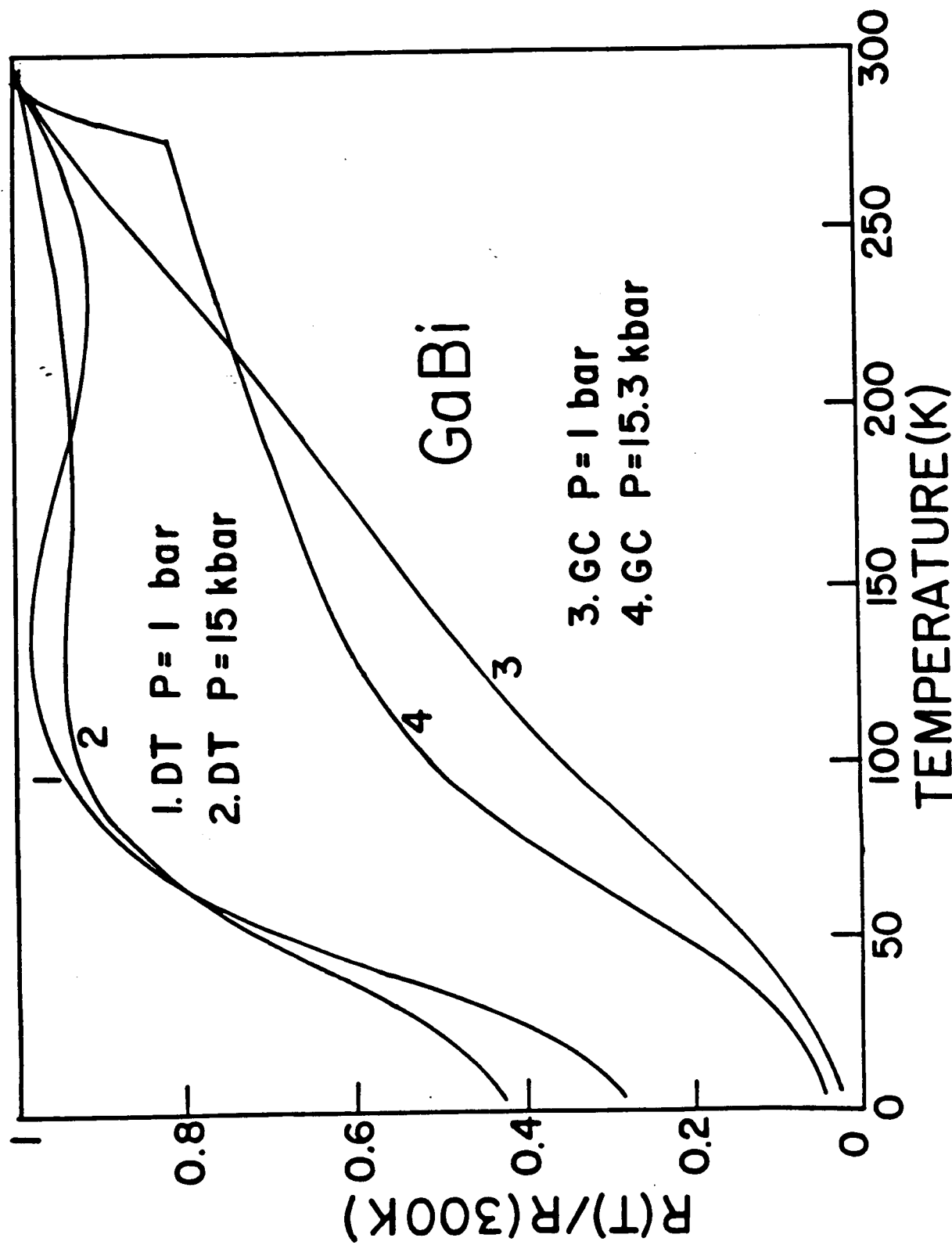


Figure 9: Temperature dependence of resistance of DT and GC GaBi at two pressures. Curve 1 and 2 are for DT sample, 3 and 4 are for GC sample.

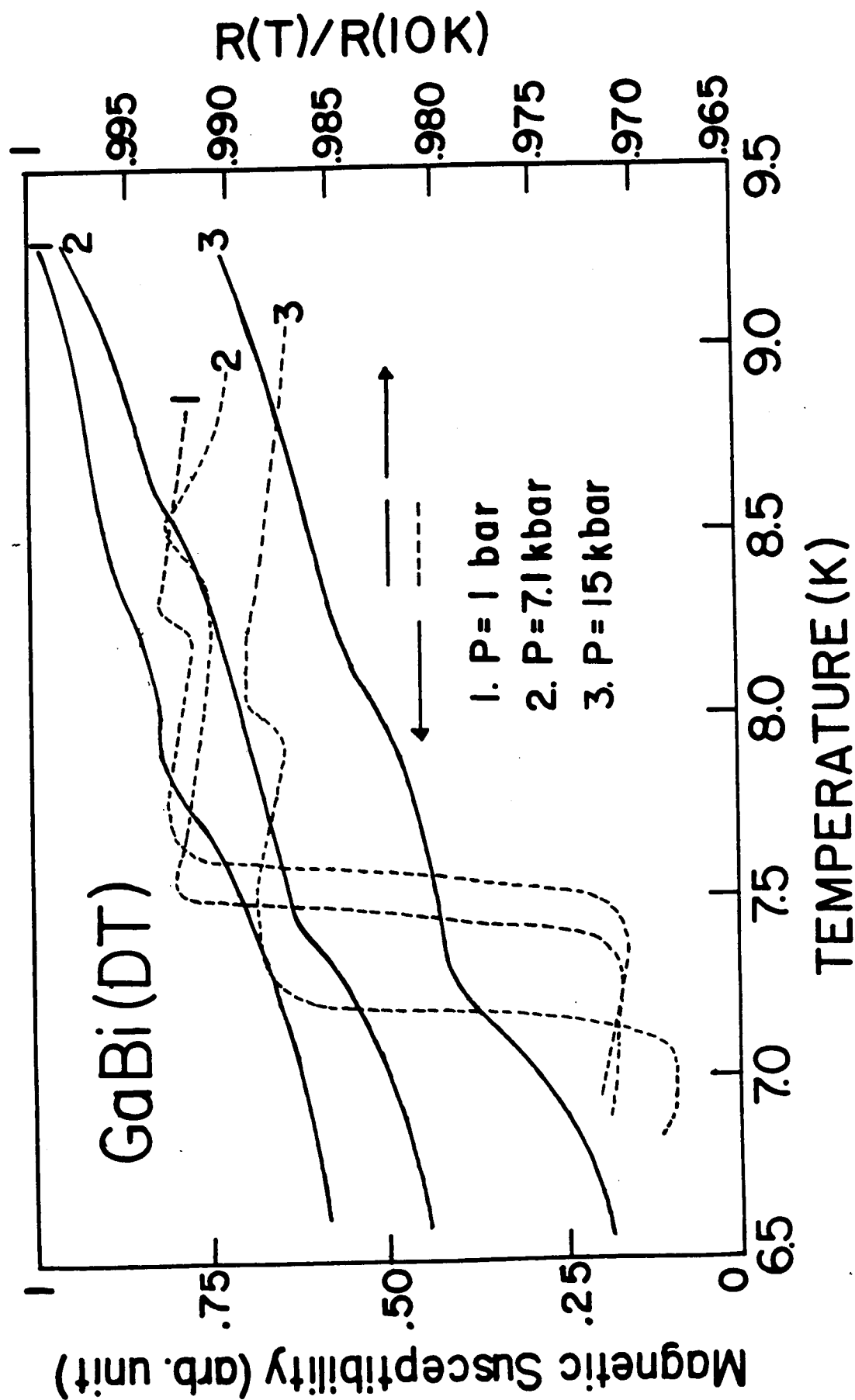


Figure 10: Low temperature electrical resistivity and magnetic susceptibility of the DT sample at three pressures. The dash line is susceptibility (left scale) and the solid line is resistivity (right scale).

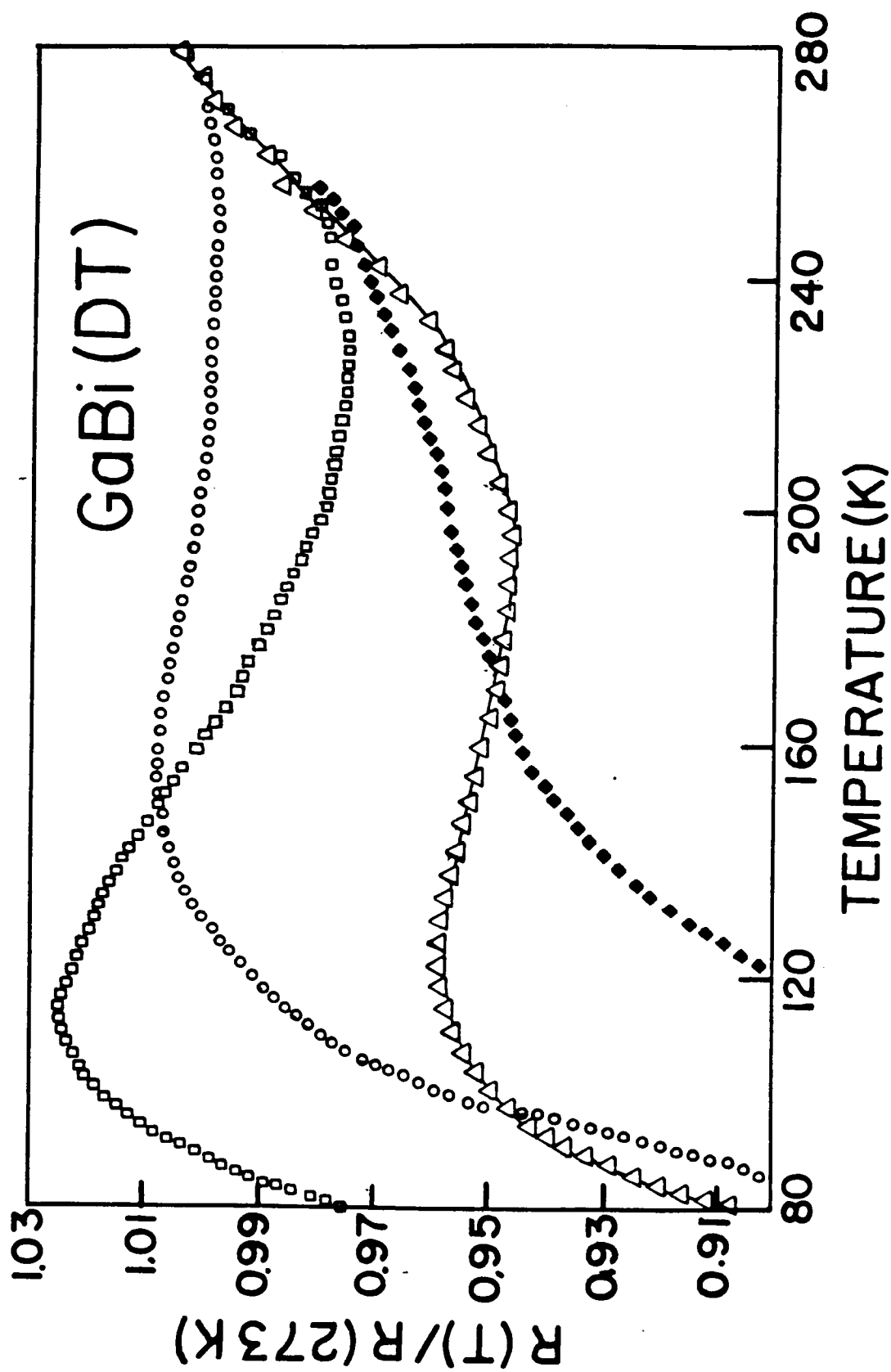


Figure 11: High temperature resistance of DT sample as a function of temperature at different pressures. Open triangle, $P=1$ bar; open square, $P=10$ kbar; open circle, $P=14.0$ kbar; solid square, $P=17.6$ kbar.

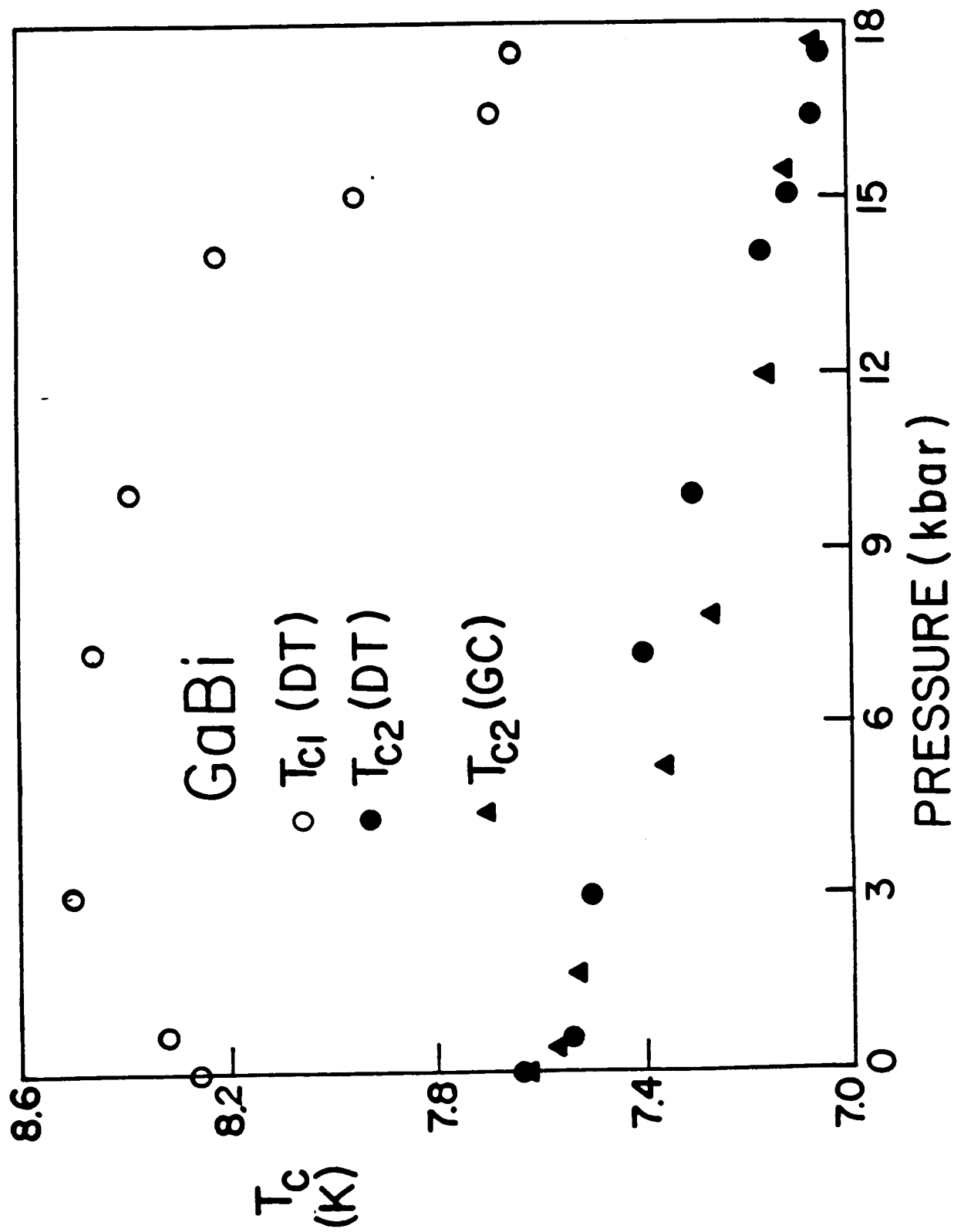


Figure 12: Superconducting transition temperature of DT and GC samples as a function of pressure.